CLAIMS

1. A process for the production of nanohybrid sol-gel materials for the heterogeneous aerobic catalysis containing tetra-*n*-propylammonium perruthenate (TPAP) entrapped in the matrix, obtained via a sol-gel process by hydrolysis and co-polymerization of organosilanes and of silanes in the presence of said tetra-*n*-propylammonium perruthenate (TPAP), water and an organic cosolvent,

characterized in that

said co-polymerization is carried out with a precursor fluorinated organosilane and a non-fluorinated silane monomer.

2. The process according to claim 1, wherein said fluorinated organosilane and said silane are in the form of metal alkoxydes.

3. The process according to claim 2, wherein said precursor fluorinated organosilane is a fluorinated silica alkoxide,

a bis-silylated alkoxide, or a fluorinated organosilane.

4. The process according to claim 3, wherein said fluorinated silica alkoxide is a compound of the formula

$$nR\text{-}Si(OCH_3)_3$$

wherein n is an integer of 1 to n, and R represents:

F- (3,fluorotrimethoxysilane),

a fluorinated alkyl chain $CF_3(CH_2)_2$-, $CF_3(CF_2)_7CH_2CH_2$-, or $CF_3(CF_2)_5CH_2CH_2$-, to form a perfluoroalkyl group,

5. The process according to claim 3, wherein said bis-silylated alkoxide is $(CH_3CH_2O)_3Si\text{-}R\text{-}Si(OCH_3CH_2)_3$ and said fluorinated organosilanes have the formula $RR'Si(OCH_3)_3$ wherein R has the meaning indicated in claim 7 and R' is any one non-hydrolyzable substituent organic group.

6. The process according to claim 5, wherein said non-hydrolyzable substituent organic group is CH_3-, CH_3CH_2-, $CH_3CH_2CH_2$- .

7. The process according to claim 1, wherein said

non-fluorinated silane monomer is $Si(OCH_3)_4$(TMOS), $Si(OCH_2CH_3)_4$(TEOS) or mixtures thereof.

8. The process according to claim 1, wherein said cosolvent is methanol, ethanol, propanol or a combination thereof.

9. The process according to any of the claims 1 to 8, wherein the molar ratio (Si:MeOH:H_2O) molar ratio among the total silica (Si) (fluorinated organosilane + silane), amount of cosolvent (MeOH), and amount of water (H_2O), is selected so as to utilize elevated stoichiometric values, both of water and of cosolvent, e.g. ranging from 1:4:4 to 1:8:8, in particular of 1:8:4, so that the resulting hydrophobic matrices of said catalysts exhibit particular reactivity.

10. A process for the production of nanohybrid sol-gel catalysts for the heterogeneous aerobic catalysis containing tetra-*n*-propylammonium perruthenate (TPAP) entrapped in the matrix, obtained via a sol-gel process by hydrolysis and co-polymerization of organosilanes and of siloxanes in the presence of said tetra-*n*-propylammonium perruthenate (TPAP), water and methanol as organic cosolvent,

characterized in that

the proportion (Si:MeOH:H_2O) of organosilane/siloxane (Si) ratio b/w, amount of cosolvent (MeOH) b/w and amount of water (H_2O) b/w, is selected so as to range from 1:8:1 to 1:4:4, so that the matrices of said catalysts have hydrophobic character.

11. The process according to claim 10, wherein said sol-gel polycondensation is carried out by adding the organosilane and the silane in a solution of TPAP in MeOH cooled in an ice bath.

12 The process according to claim 11, wherein said organosilane is selected among alkyltrimethoxysilane (RTMS), methyltrimethoxysilane (MTMS), ethyltrimethoxysilane (ETMS) propyltrimethoxysilane (PTMS) and said organosiloxane is selected between

tetramethoxyorthosilicate (TMOS) and tetraethoxyorthosilicate (TEOS).

13. A nanohybrid sol-gel catalytic material, based on silica organically modified and doped with the ruthenium species tetra-*n*-propylammonium perruthenate (TPAP) produced via a process as claimed in claims 1 to 12.

14. Use of a nanohybrid sol-gel material, based on silica organically modified and doped with the ruthenium species tetra-*n*-propylammonium perruthenate (TPAP) as claimed in claim 13, for use as catalyst having a highly efficient hydrophobic matrix for the selective aerobic oxidation of alcohols to carbonyls with oxygen at atmospheric pressure in a solvent.

15. The use of a material according to claim 14, wherein said solvent is carbon dioxide in supercritical state.

16. The use of a material according to claim 14, wherein said solvent is an organic solvent.

17. The use of a material according to claim 16, wherein said solvent is toluene or dichloromethane.

18. A process for the selective heterogeneous aerobic catalytic oxidation of alcohols to carbonyls in a solvent, wherein, as catalyst, it is employed a nanohybrid sol-gel material based on silica organically modified and doped with the ruthenium species tetra-*n*-propylammonium perruthenate (TPAP), as claimed in claim 13, and as solvent in the reaction of said catalytic oxidation it is employed carbon dioxide in supercritical state.

19. The process according to claim 18, wherein, as primary oxidant, it is employed oxygen at atmospheric pressure.

20. The process according to claim 18 or 19, wherein during the catalytic oxidation the temperature of the supercritical carbon dioxide is kept within a range of from 50° to 120°C at a pressure of from 70 to 240 bar,

and the partial pressure of the oxygen is kept at a few bars, and in particular in the neighborhood of the value of 1 bar.

21. The process according to claim 20, wherein said solvent is an organic solvent and wherein during the catalytic oxidation the temperature of the reaction mixture is kept within a range of 50° to 120°C.

22. The process according to claim 21, wherein said solvent is toluene.

23. The process according to any of the claims 18 to 22 for the heterogeneous aerobic oxidation of benzyl alcohol, 1-phenylethanol, cyclohexanol, 1-octanol, trans-cinnamyl alcohol.

24. Nanohybrid sol-gel catalyst for the heterogeneous aerobic catalysis containing tetra-*n*-propylammonium perruthenate (TPAP) entrapped in the sol-gel matrix obtained by a process as claimed in any one of claims 18 to 23.

25. Alcohol oxidation product obtained by a process as claimed in any one of claims 18 to 23.